

Two-dimensional femtosecond vibrational spectroscopy of liquids

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The nonlinear optical response of liquids subjected to a series of N femtosecond laser pulses is calculated using a multimode harmonic model for nuclear motions, with nonlinear coupling to the radiation field through the coordinate dependence of the electronic polarizability. Using electronically off-resonant optical fields, this multidimensional spectroscopy is shown to provide direct information regarding the homogeneous or the inhomogeneous nature of the spectral density obtained from optical birefringence measurements. Complementary information can be obtained using infrared pulses where the multiple time correlation functions of the nuclear dipole moment (rather than the electronic polarizability) are being probed.

I. INTRODUCTION

The interpretation of vibrational line shapes in liquids has been the subject of numerous experimental and theoretical studies.¹⁻³ Dephasing processes are crucial for the interpretation of optical processes in condensed phases. These processes are traditionally classified as either homogeneous or inhomogeneous.⁴⁻⁶ When different molecules have different transition frequencies because of varying local environments or initial states, the spectral line shape is said to be inhomogeneously broadened. This broadening carries no dynamical information. Homogeneous broadening arises from an interaction with a bath with a very fast time scale, causing rapid fluctuations in the local environment. Since nuclear motions in liquids cover a broad range of time scales, it is not clear whether spectral line shapes can be classified as either homogeneous or inhomogeneous. Even when such classification is possible by virtue of separation of time scales, it is not easy to firmly establish it experimentally.

Linear optical measurements result in a line shape that is a simple convolution of the homogeneous and the inhomogeneous contributions, and they cannot therefore distinguish between the two mechanisms. Nonlinear techniques such as fluorescence line narrowing, hole burning, and photon echoes are, however, sensitive to this distinction.⁷⁻⁹ Early off-resonant picosecond coherent Raman measurements were assumed to have the capacity of selectively eliminating inhomogeneous vibrational dephasing and revealing the homogeneous component.^{1,10-12} Loring and Mukamel¹³ have formulated the problem using a multitime correlation function approach and showed that this electronically off-resonant Raman technique, which contains only a single time variable is equivalent to linear absorption and is thus nonselective in principle. They pointed out that only multitime techniques such as the Raman echo can probe selectively the homogeneous linewidth. Several experiments have been subsequently carried out in order to measure the homogeneous vibrational linewidth.¹⁴⁻¹⁷ These experiments were conducted on isolated intramolecular high frequency vibrations and employed laser pulses longer than the vibrational periods. As such they did not have the time resolution to observe directly the vibrational motions.

The decay of the signal with the delay between the excitation and the probe pulses then reflects vibrational dephasing.

Recent development of femtosecond techniques made it possible to probe intermolecular vibrations in the frequency range 0–700[cm^{-1}] using an impulsive excitation with pulses short compared with the vibrational periods.¹⁸⁻²³ Under these conditions the time resolved signal can show the coherent vibrations as well as their dephasing. Experiments conducted so far including impulsive Raman, optical Kerr, and pump-probe spectroscopy have yielded spectral densities in the frequency range of 0–500 cm^{-1} which provide characteristic signatures of intermolecular nuclear degrees of freedom, both local and collective. It is tempting to attribute the structure observed in these spectral densities to coherent nuclear motions, as suggested by instantaneous normal mode descriptions of liquids.²⁴⁻²⁷ However, since impulsive birefringence and stimulated Raman techniques have only a single time variable, the limitations of the picosecond Raman measurements apply here as well; it is impossible to deconvolute the inhomogeneous contributions to these spectral densities, and higher order measurements are called for.

In this article we employ path-integral techniques²⁸ to derive a closed form expression for the nuclear response function to an arbitrary order in the field, using a harmonic model for nuclear motions with a nonlinear coupling to the radiation field (i.e., through the nonlinear dependence of the electronic polarizations on nuclear coordinates). Inhomogeneous broadening is incorporated by using a multimode Brownian oscillator model⁷ and assuming a static distribution of its parameters. As an illustration we analyze the possible application of a five-pulse ($P^{(5)}$) measurement to a model liquid with a typical optical birefringence spectral density. Adopting a correlation function terminology, an off-resonant $P^{(3)}$ measurement such as CARS is related to a two-time correlation function of the nuclear polarization with a single propagation period and, as far as the nuclear dynamics are concerned, is equivalent to linear absorption. Higher order techniques $P^{(5)}$, $P^{(7)}$, etc., can provide valuable additional information. By looking at the joint dynamics of N evolution periods we have in effect an N dimensional spectroscopy. Two-dimensional spectroscopy.

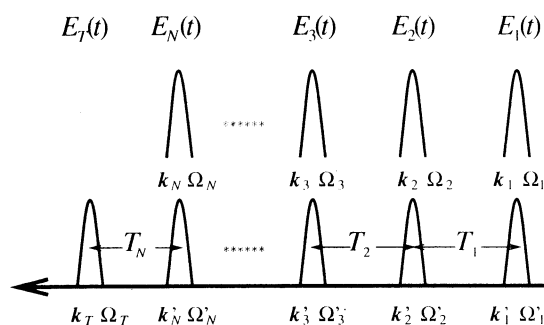


FIG. 1. Pulse configuration for a $2N+1$ th order experiment. The system first interacts with N pairs of pulses, which have the same time profile $E_j(t)$, but different wave vectors \mathbf{k}_j and \mathbf{k}'_j and frequencies Ω_j and Ω'_j for the j th pair of pulses, respectively. The last pulse (\mathbf{k}_T, Ω_T) is the probe that generates the signal.

copy has proven extremely valuable in the analysis of NMR spectra of complex systems such as proteins.²⁹ The present analysis has some close connection with its NMR counterpart, although the type of information obtained here is very different, and nuclear systems are much more complicated than spin systems. The present theory applies also to experiments conducted using resonant infrared (rather than off-resonant optical) laser pulses. Comments to that effect will be made in the discussion.

In Sec. II, we formulate the vibrational polarizations in the ground state using path integral techniques. In Sec. III, we calculate the $2N+1$ th order off-resonant response functions for a single harmonic oscillator system. We then extend these results to a multimode damped oscillator system in Sec. IV. In Sec. V we show how the multidimensional spectrum can be used to distinguish between homogeneous and inhomogeneous line broadening mechanisms by calculating fifth order off-resonant signals. Concluding remarks are made in Sec. VI.

II. VIBRATIONAL POLARIZATION IN THE GROUND STATE

Consider a liquid system interacting with an external electric field. The Hamiltonian is

$$H = H_0 - E(\mathbf{r}, t)V, \quad (2.1)$$

where H_0 is the electronic and nuclear Hamiltonian of the liquid and V represents its interaction with the electric field. The external field consists of a train of N pairs of simultaneous pulses, followed by a final (probe) pulse, (Fig. 1)

$$E(\mathbf{r}, t) = \sum_{j=1}^N E_j(\mathbf{r}, t) + E_T(\mathbf{r}, t), \quad (2.2)$$

where

$$E_j(\mathbf{r}, t) = E_j(t) \{ \exp[i(\Omega_j t - \mathbf{k}_j \mathbf{r})] + \exp[i(\Omega'_j t - \mathbf{k}'_j \mathbf{r})] \} + \text{c.c.}, \quad (2.3)$$

and

$$E_T(\mathbf{r}, t) = E_T(t) \exp[i(\Omega_T t - \mathbf{k}_T \mathbf{r})] + \text{c.c.} \quad (2.4)$$

Here $E_j(t)$ denotes the temporal profile of the j th pulse. We assume that the pulse pairs are well separated in time. We further assume that the system is initially in thermal equilibrium in the ground electronic state.

Femtosecond measurements conducted with laser fields tuned far below any electronic transition provide valuable information regarding nuclear motions.¹⁸⁻²³ Off-resonant measurements have the following attractive characteristics. (i) Excited state populations are limited by the Heisenberg relation to very short times $\Delta t \approx 1/\Delta\omega$, $\Delta\omega$ being the off-resonant detuning. As $\Delta\omega$ is increased, these populations become practically negligible and the measurements probe only ground state dynamics. (ii) The time the system spends in an electronic coherence is also limited by the same Heisenberg relation, and consequently, nuclear dynamics can be neglected during coherence periods. In an experiment conducted with $2N+1$ laser pulses, related to the polarizations $P^{(2N+1)}$, we need to consider therefore only N (rather than $2N$) time evolution periods, in which the system is in the ground state. The above arguments greatly simplify the interpretation of these measurements. On the other hand, simplifying assumptions such as the rotating wave approximation and the independence of the dipole moment on nuclear coordinates (the Condon approximation) which usually hold in resonant measurements cannot be justified under off resonant conditions.

Because of (i) and (ii), the electronic excited states do not play a role in the off-resonant experiments, and we can describe the system by an effective ground state nuclear Hamiltonian,^{7,30} where all electronic excited states have been eliminated,

$$H = H_g(\mathbf{p}, \mathbf{q}) - E^2(\mathbf{r}, t)\alpha(\mathbf{q}), \quad (2.5)$$

where $\alpha(\mathbf{q})$ is the electronic polarizability. A derivation of this effective Hamiltonian starting with a two electron level system is given in Appendix A. The form Eq. (2.5) applies, however, to a system with an arbitrary number of electronically excited states. For clarity, we hereafter assume that the polarizability is isotropic, and do not use an explicit tensor notation; this can be incorporated with no major difficulty.²⁰ The $2N+1$ th polarization is then expressed as

$$P^{(2N+1)}(t) = 2^{N+1} E_T(t) \exp(i\Omega_T t - i\mathbf{k}_T \mathbf{r}) \times \left\{ \prod_{j=1}^N \int_0^\infty d\tau_j E_j^2 \left(t - \sum_{k=j}^N \tau_k \right) \times \left[\cos \left(\Delta\Omega_j \left(t - \sum_{k=j}^N \tau_k \right) - \Delta\mathbf{k}_j \mathbf{r} \right) + 1 \right] \right\} \times R^{(2N+1)}(\{\tau_j\}), \quad (2.6)$$

where the $2N+1$ th order response function is given by

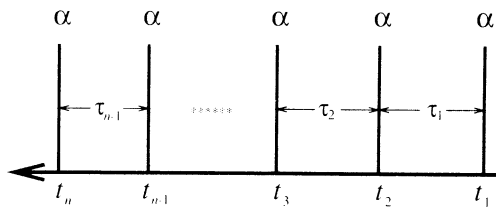


FIG. 2. Time variables for the N th order response function [Eq. (2.7)]. In the figure, t_j are the times of the actual interactions with the fields and τ_j are the intervals between successive interactions.

$$R^{(2N+1)}(\{\tau_j\}) \equiv \left(\frac{i}{\hbar}\right)^N \text{tr} \left\{ \alpha(\mathbf{q}) \left[\prod_{j=1}^N \exp\left(-\frac{i}{\hbar} H_g^\times \tau_j\right) \alpha^\times(\mathbf{q}) \right] \rho_g \right\}. \quad (2.7)$$

Here $\alpha^\times A \equiv [\alpha, A]$ represents the commutator with the electronic polarizability. This response function depends only on the ground electronic state dynamics. The laser pulses thus enter as an external driving force for the nuclear degrees of freedom, and the coupling is proportional to the electronic polarizability. Since each α^\times can act either from the left or from the right, the above expression contains 2^N terms. For example, the two lowest order response functions are written as

$$R^{(3)}(\tau_1) = \frac{i}{\hbar} \langle [\alpha(t_2), \alpha(t_1)] \rho_g \rangle, \quad (2.8)$$

$$R^{(5)}(\tau_2, \tau_1) = -\frac{1}{\hbar^2} \langle [[\alpha(t_3), \alpha(t_2)], \alpha(t_1)] \rho_g \rangle, \quad (2.9)$$

where $\alpha(t_j)$ represents the operator $\alpha(\mathbf{q})$ in the interaction picture at time $t_j = \sum_{k=j}^N \tau_k$, (Fig. 2)

$$\alpha(t_j) \equiv \exp(iH_g t_j) \alpha(\mathbf{q}) \exp(-iH_g t_j). \quad (2.10)$$

We can calculate all of these terms using a Liouville space generating function.²⁸ A typical term in Eq. (2.9), for example, can be written as

$$\langle \alpha(t_2) \alpha(t_3) \alpha(t_1) \rho_g \rangle = \lim_{\mathbf{a} \rightarrow 0} \{ \hat{\alpha}_1 \hat{\alpha}_2 \hat{\alpha}_3 F(\mathbf{a}; t) \}. \quad (2.11)$$

Here

$$\hat{\alpha}_j \equiv \alpha \left(\frac{\partial}{\partial a_j} \right), \quad (2.12)$$

$$F(\mathbf{a}; t) \equiv \text{tr} \left\{ \exp \left[-\frac{i}{\hbar} \int_0^t dt (H_g(\mathbf{p}, \mathbf{q}) + V(t) \mathbf{q}) \right] \times \exp[-\beta H_g(\mathbf{p}, \mathbf{q})] \exp \left[\frac{i}{\hbar} \int_0^t dt (H_g(\mathbf{p}, \mathbf{q}) + V'(t) \mathbf{q}) \right] \right\}, \quad (2.13)$$

with

$$V(t) = -i\hbar [a_1 \delta(t-t_1) + a_3 \delta(t-t_3)], \quad (2.14)$$

$$V'(t) = i\hbar a_2 \delta(t-t_2),$$

and $\mathbf{a} \equiv \{a_1, a_2, a_3\}$, and $\lim_{\mathbf{a} \rightarrow 0}$ indicates setting $a_j \rightarrow 0$ after performing the derivative $\alpha(\partial/\partial a_j)$. In a similar way, we can define generating functions to any order $F^{(2N+1)}(\mathbf{a}; t)$, where $\mathbf{a} = \{a_1, a_2, a_3, \dots, a_{N+1}\}$.

III. RESPONSE FUNCTIONS OF A SINGLE HARMONIC NUCLEAR MODE

We shall now apply our results to a model system with a single nuclear degree of freedom. The generalization to an arbitrary number of degrees of freedom is straightforward and will be made in the Sec. IV. We thus take for the ground state Hamiltonian

$$H_g(p, q) = p^2/2m + \frac{1}{2} m \omega_0^2 q^2. \quad (3.1)$$

The calculation of $F(\mathbf{a}; t)$ is formally identical to the Feynman-Vernon influence functional,³¹ although the underlying physics are very different, since $V(t)$ in our case is an external given function, that does not depend on the system coordinate. We then have

$$F(\mathbf{a}; t) = \exp \left[-\frac{1}{2\hbar m \omega_0} \int_0^t d\tau' \int_0^{\tau'} d\tau (V(\tau') - V'(\tau')) \left(\cos(\omega_0(\tau' - \tau)) \coth\left(\frac{\beta\hbar\omega_0}{2}\right) \times (V(\tau) + V'(\tau)) - i \sin(\omega_0(\tau' - \tau)) \times (V(\tau) - V'(\tau)) \right) \right]. \quad (3.2)$$

The generating force $V(t)$ for the $2N+1$ th order response function can be defined by introducing the sign operators ϵ_j , where $\epsilon_j = -$ if α_j operates on ρ from the left and $\epsilon_j = +$ for operation from the right. Each of the possible 2^N Liouville space paths can thus be defined by a special choice of ϵ_j ($j=1, \dots, N$). For the last interaction we always set $\epsilon_{N+1} = -$. Using this notation we have

$$V(t) - V'(t) = -i\hbar \sum_{j=1}^{N+1} a_j \delta \left(t - \sum_{k=1}^j \tau_k \right), \quad (3.3)$$

$$V(t) + V'(t) = -i\hbar \sum_{j=1}^{N+1} \epsilon_j a_j \delta \left(t - \sum_{k=1}^j \tau_k \right).$$

The $2N+1$ th generating function is then given by

$$F^{(2N+1)}(\mathbf{a}; \{\tau_j\}) = \exp \left[\sum_{j=k+1}^{N+1} \sum_{k=1}^N a_j a_k C_{-\epsilon_k} \left(\sum_{m=k}^j \tau_m \right) + \frac{1}{2} \sum_{j=1}^{N+1} a_j^2 C'(0) \right], \quad (3.4)$$

where $C_{\pm}(t)$ are the two-time autocorrelation functions of the nuclear coordinate ($C_+(t) \equiv \langle q(t)q \rangle$, $C_-(t) \equiv \langle q(q(t)) \rangle$) defined by

$$C_{\pm}(t) \equiv \frac{\hbar}{2m\omega_0} \left[\cos(\omega_0 t) \coth\left(\frac{\beta\hbar\omega_0}{2}\right) \pm i \sin(\omega_0 t) \right], \quad (3.5)$$

and $C'(t)$ is the real part of $C_{\pm}(t)$. We finally have for the $2N+1$ th order response function

$$R^{(2N+1)}(\{\tau_j\}) = \lim_{\hbar \rightarrow 0} \left(\frac{i}{\hbar} \right)^N \sum_{\epsilon_1=\pm} \sum_{\epsilon_2=\pm} \cdots \sum_{\epsilon_N=\pm} \epsilon_1 \epsilon_2 \cdots \epsilon_N \\ \times \hat{\alpha}_1 \hat{\alpha}_2 \cdots \hat{\alpha}_{N+1} F^{(2N+1)}(\mathbf{a}; \{\tau_j\}). \quad (3.6)$$

The nonlinear response function can be interpreted in terms of the time evolution of nuclear wavepackets in phase space.^{7,28} Each Liouville pathway has its own wave packet which serves as a generating function for the optical response. Since the response function is given by the trace of the wave packet, it is not essential to calculate the wave packets. They provide, however, a clear semiclassical picture of the optical response. For the present harmonic model, these wave packets are Gaussian and are given in Appendix B. For more complex (anharmonic) models they can be calculated numerically using classical trajectories.

We next apply these results to two and three pulse experiments. From Eqs. (2.6), (3.4), and (3.6), the third order polarization is given by

$$P^{(3)}(t) = 2^2 \int_0^\infty d\tau_1 E_T(t) E_1^2(t-\tau_1) \exp(i\Omega_T t - i\mathbf{k}_T \mathbf{r}) \\ \times [\cos(\Delta\Omega_1(t-\tau_1) - \Delta\mathbf{k}_1 \mathbf{r}) + 1] R^{(3)}(\tau_1). \quad (3.7)$$

The response function is calculated using the generating function

$$R^{(3)}(\tau_1) = \lim_{\hbar \rightarrow 0} \frac{i}{\hbar} \sum_{\epsilon_1=\pm} \epsilon_1 \hat{\alpha}_1 \hat{\alpha}_2 F^{(3)}(\mathbf{a}; \tau_1), \quad (3.8)$$

with

$$F^{(3)}(\mathbf{a}; \tau_1) = \exp[a_2 a_1 C_{-\epsilon_1}(\tau_1) + \frac{1}{2}(a_1^2 + a_2^2) C'(0)]. \quad (3.9)$$

The fifth-order polarization is given by

$$P^{(5)}(t) = 2^3 \int_0^\infty d\tau_2 \int_0^\infty d\tau_1 E_T(t) E_2^2(t-\tau_2) E_1^2(t-\tau_2-\tau_1) \\ \times \exp(i\Omega_T t - i\mathbf{k}_T \mathbf{r}) [\cos(\Delta\Omega_2(t-\tau_2) - \Delta\mathbf{k}_2 \mathbf{r}) + 1] [\cos(\Delta\Omega_1(t-\tau_2-\tau_1) - \Delta\mathbf{k}_1 \mathbf{r}) + 1] R^{(5)}(\tau_2, \tau_1), \quad (3.10)$$

where

$$R^{(5)}(\tau_2, \tau_1) = - \lim_{\hbar \rightarrow 0} \frac{1}{\hbar^2} \sum_{\epsilon_1=\pm} \sum_{\epsilon_2=\pm} \\ \times \epsilon_1 \epsilon_2 \hat{\alpha}_1 \hat{\alpha}_2 \hat{\alpha}_3 F^{(5)}(\mathbf{a}; \tau_2, \tau_1), \quad (3.11)$$

with

$$F^{(5)}(\mathbf{a}; \tau_2, \tau_1) = \exp[a_3 a_1 C_{-\epsilon_1}(\tau_2 + \tau_1) + a_3 a_2 C_{-\epsilon_2}(\tau_2) \\ + a_2 a_1 C_{-\epsilon_1}(\tau_1) + \frac{1}{2}(a_1^2 + a_2^2 + a_3^2) \\ \times C'(0)]. \quad (3.12)$$

In Appendix C, we derive the same results starting from the $2N+1$ th order response functions for a displaced oscillator system.

It is interesting to note that if $\alpha(q)$ depends linearly on nuclear coordinates, the present model is linear and all nonlinear response functions should vanish identically. This can be easily seen from the Heisenberg equation for q , which gives

$$\dot{q} = -\omega^2 q + E(t) \quad (3.13)$$

(when a damping term $\gamma \dot{q}$ is added in the right-hand side, this is known as the Drude model). In Liouville space this is a result of an interesting interference of various paths, as will be shown below.

The simplest model which yields a finite nonlinear response is when the electronic polarization has an exponential dependence on the nuclear coordinate, i.e.,

$$\alpha(q) = \alpha_0 \exp(aq). \quad (3.14)$$

In this case, the response functions are obtained by simply setting $a_j = a$ in Eqs. (3.9) and (3.12) and no derivatives are necessary. Expanding in powers of a^2 , the lowest two terms in the third and the fifth order response functions are given by

$$R^{(3)}(\tau_1) = \frac{2}{\hbar} \alpha_0^2 a^2 C''(\tau_1) + \frac{2}{\hbar} \alpha_0^2 a^4 C'''(\tau_1) C'(\tau_1) + \cdots, \quad (3.15)$$

and

$$R^{(5)}(\tau_2, \tau_1) = \frac{4}{\hbar^2} \alpha_0^3 a^4 C''(\tau_2) [C''(\tau_1) + C''(\tau_1 + \tau_2)] \\ + \frac{4}{\hbar^2} \alpha_0^3 a^6 C''(\tau_2) [C''(\tau_1) + C''(\tau_1 + \tau_2)] \\ \times [C'(\tau_1) + C'(\tau_2) + C'(\tau_1 + \tau_2) \\ + \frac{3}{2} C'(0)] + \cdots, \quad (3.16)$$

where $C'(t)$ and $C''(t)$ are the real and the imaginary parts of $C_{\pm}(t)$, respectively. The absence of an a^3 term in $R^{(5)}$ reflects the destructive interference that eliminates the nuclear response for the linear model $\alpha = \alpha_0 a q$. Similar expressions for the seventh order response functions are given in Appendix D. Since $C''(t)$ is temperature independent and a is a small parameter (typically $a q \ll 0.1$), the temperature dependence of $R^{(3)}$ and $R^{(5)}$ is expected to be weak. The response functions for a general form of the polarizability (not necessary exponential) are given in Appendix E.

In the classical $\hbar \rightarrow 0$ limit, we have

$$C'(t) = \frac{k_B T}{m\omega_0^2} \cos(\omega_0 t), \quad (3.17)$$

$$\frac{1}{\hbar} C''(t) = \frac{1}{2m\omega_0} \sin(\omega_0 t) = -\frac{1}{2k_B T} \frac{\partial}{\partial t} C'(t).$$

The classical correlation function $C_{cl}(t)$ is equal to $C'(t)$. Using Eq. (3.17), we obtain a classical approximation for $R^{(2N+1)}$.^{8,32}

IV. HOMOGENEOUS VS INHOMOGENEOUS MULTIMODE BROWNIAN OSCILLATOR SYSTEM

The generalization of the previous results to a multimode harmonic system is straightforward. Consider the ground state Hamiltonian

$$H_g(\mathbf{p}, \mathbf{q}) = \sum_s \left(\frac{p_s^2}{2m_s} + \frac{1}{2} m_s \omega_s^2 q_s^2 \right), \quad (4.1)$$

with the electronic polarization

$$\alpha(\mathbf{q}) = \alpha_0 \exp\left(\sum_s A_s a q_s \right). \quad (4.2)$$

Here q_s are the primary oscillators that couple directly to the electronic polarizability. They can represent local or collective coordinates. A_s is the coupling constant for the α th oscillator. The dimension of A_s is chosen to be m^{-1} , therefore, a is a dimensionless coupling parameter. In this case, the generating functions are expressed as

$$F^{(2N+1)}(a; \{\tau\}) = \prod_s F_s^{(2N+1)}(a; \{\tau\}), \quad (4.3)$$

where

$$F_s^{(2N+1)}(a; \{\tau\}) = \exp \left[a^2 \sum_{j=k+1}^{N+1} \sum_{k=1}^N C_{-\epsilon_k}^s \left(\sum_{m=k}^j \tau_m \right) + \frac{1}{2} a^2 \sum_{j=1}^{N+1} C'^s(0) \right]. \quad (4.4)$$

The correlation function for the s th mode is now given by

$$C_{\pm}^s(t) = \int d\omega \mathcal{F}(\omega) \left[\cos(\omega t) \coth\left(\frac{\beta \hbar \omega}{2}\right) \pm i \sin(\omega t) \right], \quad (4.5)$$

where

$$\mathcal{F}(\omega) = (\eta_s / 2\omega_s) \delta(\omega - \omega_s). \quad (4.6)$$

We next assume that each nuclear mode is coupled to an environment consisting of a set of bath harmonic oscillators with coordinates x_k^s and momenta p_k^s .³³⁻³⁵ The interaction between the system and the k th bath oscillator is assumed to be linear with a coupling strength c_k^s . The total Hamiltonian is then given by,

$$H_g(\mathbf{p}, \mathbf{q}) = \sum_s \left\{ \frac{p_s^2}{2m_s} + \frac{1}{2} m_s \omega_s^2 q_s^2 + \sum_k \left[\frac{(p_k^s)^2}{2m_k^s} + \frac{m_k^s (\omega_k^s)^2}{2} \left(x_k^s - \frac{c_k^s q_s}{m_k^s (\omega_k^s)^2} \right)^2 \right] \right\}. \quad (4.7)$$

By tracing over the nuclear and the bath coordinates, we obtain the distribution function for the s th mode in the form²⁸

$$\mathcal{F}(\omega) = \frac{1}{2\pi} \frac{\omega \eta_s \gamma_s(\omega)}{(\omega_s^2 - \omega^2)^2 + \omega^2 \gamma_s^2(\omega)}, \quad (4.8)$$

where

$$\gamma_s(\omega) \equiv \sum_k \frac{(c_k^s)^2}{2m_k^s (\omega_k^s)^2} \delta(\omega - \omega_k^s). \quad (4.9)$$

The corresponding generating function is obtained from Eq. (4.4) by replacing Eq. (4.6) by Eq. (4.8). Assuming a frequency-independent damping $\gamma_s(\omega) = \gamma_s$, which represents a Gaussian white noise on the nuclear system, we may rewrite Eq. (4.8) as

$$\sum_s \mathcal{F}(\omega) \rightarrow J(\omega; \Gamma) = \sum_s \eta_s f(\omega; \omega_s, \gamma_s), \quad (4.10)$$

where $\Gamma \equiv \{\eta_s, \omega_s, \gamma_s\}$ represents the parameters of the model, namely, the strength of the interaction (η_s), the frequency (ω_s), and the relaxation rate (γ_s) of the s th mode and

$$f(\omega; \omega_s, \gamma_s) = \frac{1}{2\pi} \frac{\omega \gamma_s}{(\omega_s^2 - \omega^2)^2 + \omega^2 \gamma_s^2}. \quad (4.11)$$

The coupling strength is given by

$$\eta_s \equiv \frac{\hbar A_s^2}{m_s}. \quad (4.12)$$

This model can be used to describe specific coordinates whether local (e.g., intramolecular) or collective in nature.⁸ Even if we do not have a clear idea of the nature of the modes of the system, it can be used as a convenient parametrization. In the liquid phase,^{8,16,25-27,36} the distribution of the values of $\{\eta_s, \omega_s, \gamma_s\}$ may reflect different slowly interconverting local environments. Similar problems of inhomogeneity are of current interest in the studies of dissipative kinetics observed in charge transfer in the photosynthetic reaction center.^{37,38} To emphasize the parametric dependence on Γ , we change the notation $J(\omega)$ to $J(\omega; \Gamma)$ and $R^{(2N+1)}(\{\tau_j\})$ to $R^{(2N+1)}(\{\tau_j\}, \Gamma)$. The correlation functions are then given by

$$C_{\pm}(t; \Gamma) \equiv \int d\omega J(\omega; \Gamma) \left[\cos(\omega t) \coth\left(\frac{\beta \hbar \omega}{2}\right) \pm i \sin(\omega t) \right]. \quad (4.13)$$

The dependence of Γ on nuclear configuration introduces an inhomogeneous contribution to the response

function. That dependence can be taken into account by averaging over the distribution function of the parameters $S(\Gamma)$, i.e.,

$$R^{(2N+1)}(\{\tau\}) = \int d\Gamma S(\Gamma) R^{(2N+1)}(\{\tau\}; \Gamma), \quad (4.14)$$

where

$$\begin{aligned} R^{(2N+1)}(\{\tau\}; \Gamma) &= \alpha_0^{2N-1} \left(\frac{i}{\hbar} \right)^N \sum_{\epsilon_1 = \pm} \sum_{\epsilon_2 = \pm} \cdots \sum_{\epsilon_N = \pm} \epsilon_1 \epsilon_2 \cdots \epsilon_N \\ &\times \exp \left[a^2 \sum_{j=k+1}^{N+1} \sum_{k=1}^N C_{-\epsilon_k} \left(\sum_{m=k}^j \tau_m; \Gamma \right) \right. \\ &\left. + \frac{1}{2} a^2 \sum_{j=1}^{N+1} C'(0; \Gamma) \right]. \end{aligned} \quad (4.15)$$

By using Eqs. (3.15) and (3.16), this gives for the third and the fifth order response functions

$$R^{(3)}(\tau_1) = \frac{2}{\hbar} \alpha_0^2 a^2 \int d\Gamma S(\Gamma) C''(\tau_1; \Gamma), \quad (4.16)$$

and

$$\begin{aligned} R^{(5)}(\tau_2, \tau_1) &= \frac{4}{\hbar^2} \alpha_0^3 a^4 \int d\Gamma S(\Gamma) C''(\tau_2; \Gamma) [C''(\tau_1; \Gamma) \\ &+ C''(\tau_1 + \tau_2; \Gamma)], \end{aligned} \quad (4.17)$$

where we have neglected terms higher order in a^2 .

V. IMPULSIVE EXPERIMENTS

The fifth order off-resonant experiment may be used to distinguish between the homogeneous and the inhomogeneous contributions to the spectral density observed in birefringence $R^{(3)}$ experiments. Consider the following form for the birefringence (Kerr) amplitude

$$R^{(3)}(\tau_1) = \frac{2}{\hbar} \alpha_0^2 a^2 \int d\Gamma S(\Gamma) \int d\omega J(\omega; \Gamma) \sin(\omega \tau_1), \quad (5.1)$$

where

$$\begin{aligned} R^{(3)}(\omega) &\equiv \int d\tau_1 e^{i\omega \tau_1} R^{(3)}(\tau_1) \\ &= \frac{\omega A_1 C_1}{2\pi [(B_1^2 - \omega^2)^2 + \omega^2 C_1^2]} \\ &+ \frac{\omega A_2 C_2}{2\pi [(B_2^2 - \omega^2)^2 + \omega^2 C_2^2]}. \end{aligned} \quad (5.2)$$

Here A_1 , B_1 , C_1 , etc., are chosen to represent the experimental birefringence spectral density of CH_3CN of these parameters (in $[\text{cm}^{-1}]$) are given by (see Fig. 3)²⁰

$$\begin{aligned} A_1 &= 0.01, & B_1 &= 50, & C_1 &= 100, \\ A_2 &= 0.04, & B_2 &= 350, & C_2 &= 25. \end{aligned} \quad (5.3)$$

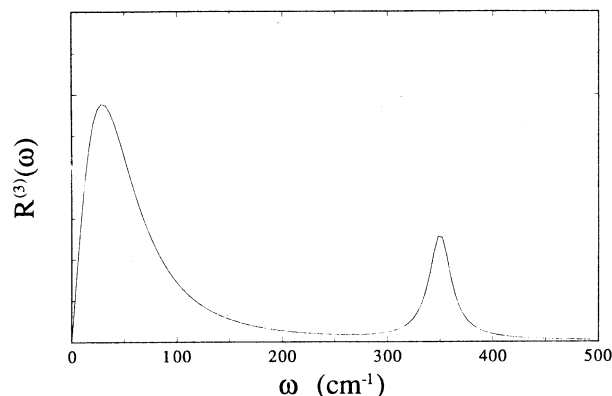


FIG. 3. The spectral distribution $R^{(3)}(\omega)$ of CH_3CN obtained from the optical Kerr experiment (Ref. 20).

$R^{(3)}$ depends on the homogeneous J and inhomogeneous S components only through the combination

$$\int d\Gamma S(\Gamma) J(\omega; \Gamma). \quad (5.4)$$

There are therefore infinite number of choices of inhomogeneous distribution $S(\Gamma)$ and homogeneous spectral distribution $J(\omega; \Gamma)$, that give the same optical Kerr signal (Fig. 4),

$$I^{(3)}(T_1) = |R^{(3)}(T_1)|^2, \quad (5.5)$$

where $R^{(3)}$ is given by Eq. (5.2). Hereafter we adopt the two extreme choices; (i) a purely homogeneous two oscillator case, where the spectral density is attributed to the two oscillator modes

$$S(\Gamma_1, \Gamma_2) = \prod_{\alpha=1}^2 \delta(\eta_{\alpha} - A_{\alpha}) \delta(\omega_{\alpha} - B_{\alpha}) \delta(\gamma_{\alpha} - C_{\alpha}), \quad (5.6)$$

$$J(\omega; \Gamma_1, \Gamma_2) = \eta_1 f(\omega; \omega_1, \gamma_1) + \eta_2 f(\omega; \omega_2, \gamma_2); \quad (5.7)$$

(ii) purely inhomogeneous one oscillator case, where a single harmonic frequency is inhomogeneously distributed

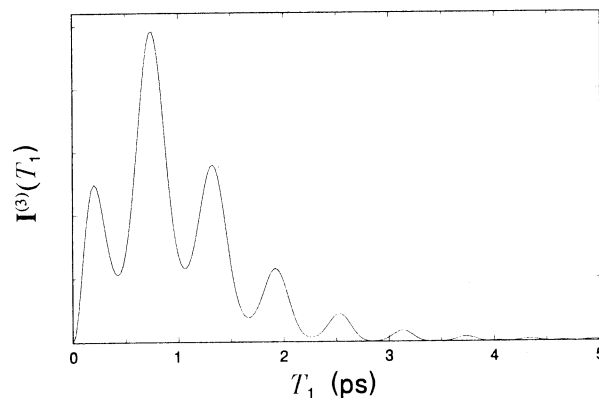


FIG. 4. The optical Kerr signal $I^{(3)}(T_1)$ for the system of Fig. 3. This experiment is not sensitive to the homogeneous or inhomogeneous nature of the spectral density.

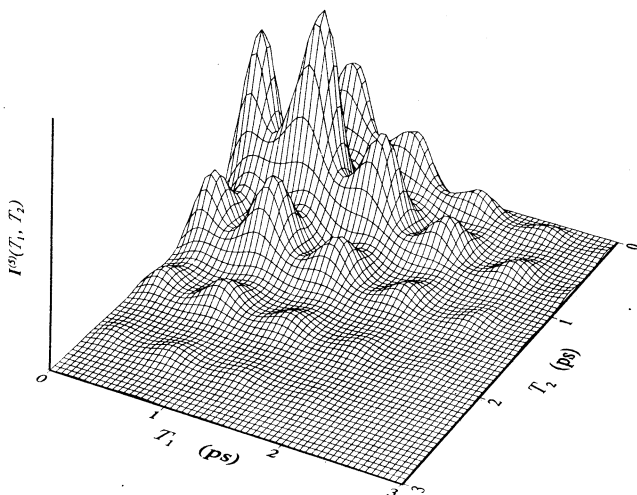


FIG. 5. The time domain 2D signal $I^{(5)}(T_1, T_2)$ for the pure homogeneous case (i) using the spectral distribution of Fig. 4.

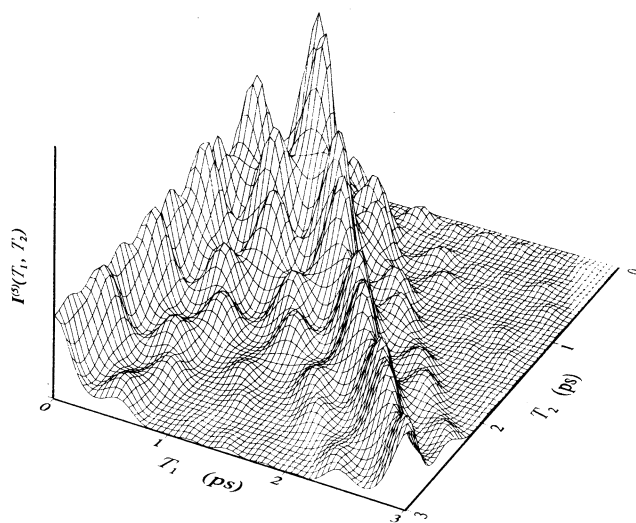


FIG. 6. The time domain 2D signal $I^{(5)}(T_1, T_2)$ for the pure inhomogeneous case (ii) using the spectral distribution of Fig. 4.

$$S(\Gamma_1) = \lim_{\epsilon \rightarrow 0} \delta(\eta_1 - 1) \delta(\gamma_1 + \epsilon) [A_1 f(\omega_1; B_1, C_1) + A_2 f(\omega_1; B_2, C_2)], \quad (5.8)$$

$$J(\omega; \Gamma_1) = \eta_1 f(\omega; \omega_1, \gamma_1). \quad (5.9)$$

As can be seen from Eq. (5.1), the third order signal, which corresponds to the optical Kerr (birefringence) experiments, is identical for the two models. This is in agreement with our previous analysis to the effect that we cannot distinguish between homogeneous and inhomogeneous contributions from experiments based on the third order response function.

Let us consider now the fifth order signal. The fifth order off-resonant response function is given by

$$R^{(5)}(\tau_2, \tau_1) = \frac{4\alpha_0^3 a^4}{\hbar^2} \int d\Gamma S(\Gamma) C''(\tau_2; \Gamma) [C''(\tau_1; \Gamma) + C''(\tau_1 + \tau_2; \Gamma)], \quad (5.10)$$

or alternatively,

$$R^{(5)}(\tau_2, \tau_1) = \frac{4}{\hbar^2} \alpha_0^3 a^4 \int d\Gamma S(\Gamma) \times \left[\int d\omega' J(\omega'; \Gamma) \sin(\omega' \tau_2) \right] \times \left[\int d\omega J(\omega; \Gamma) [\sin(\omega \tau_1) + \sin(\omega(\tau_1 + \tau_2))] \right]. \quad (5.11)$$

For impulsive pump probe experiments, such that $E_T(t) = \delta(t - T_1 - T_2)$, $E_1(t) = \delta(t)$, and $E_2(t) = \delta(t - T_1)$ for the fifth order, we can perform the time integrations over τ_j . Then the total signal intensity related the square of the polarization is given by (up to a proportionality constant)

$$I^{(5)}(T_1, T_2) = |R^{(5)}(T_2, T_1)|^2. \quad (5.12)$$

$R^{(5)}$ depends on $J(\omega; \Gamma)$ and $S(\Gamma)$ separately and not merely through the combination Eq. (5.4). This opens up the possibility of observing the difference between the homogeneous and the inhomogeneous contributions to the spectral density obtained from birefringence $R^{(3)}$ experiments (Figs. 5 and 6). The two models Eq. (5.6) together with Eq. (5.7) or Eq. (5.8) together with Eq. (5.9) have dramatically different predictions for $R^{(5)}$. This is illustrated in the following numerical calculations. For (i) the pure homogeneous and (ii) the pure inhomogeneous cases. As seen from the figures, the fifth order (3-pulse) signal is very different for the two cases. The $I^{(5)}(T_1 T_2)$ signal constitutes a two-dimensional spectroscopy with two independent time periods during which the nuclear coherence evolves.

A different perspective on these results can be obtained by performing two-dimensional (2D) Fourier transformation, as follows:^{29,39}

$$I^{(5)}(\omega_1, \omega_2) = \left| \int_0^\infty dT_1 \int_0^\infty dT_2 e^{i\omega_1 T_1 + i\omega_2 T_2} \times I^{(5)}(T_1, T_2) \right|^2. \quad (5.13)$$

Calculations were made using a two-dimensional fast Fourier transform (FFT) routine on a 256 by 256 grid. Figures 7 and 8 show, respectively, the 2D Fourier transform of (i) the pure homogeneous (Fig. 5) and (ii) the pure inhomogeneous cases (Fig. 6). In Fig. 7, we observe peaks whose positions are determined by the products $[\sin(\omega_a T_2) + \sin(\omega_b T_2)][\sin(\omega_a T_1) + \sin(\omega_b T_1)]$ and $[\sin(\omega_a T_2) + \sin(\omega_b T_2)]\{\sin[\omega_a(T_1 + T_2)] + \sin[\omega_b(T_1 + T_2)]\}$, however, since their spectral width at $(\omega_1, \omega_2) = (\pm 50, \pm 50)$ [cm^{-1}] are broad ($\gamma_a = 100$ [cm^{-1}]), we cannot distinguish them from the zero frequency peak at $(\omega_1, \omega_2) = (0, 0)$. In

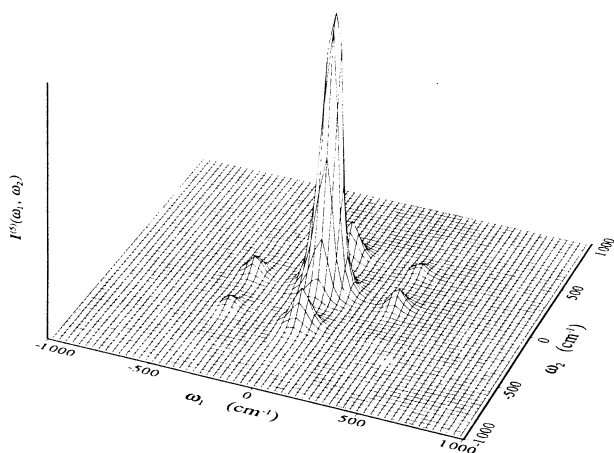


FIG. 7. The frequency domain 2D signal $I^{(5)}(\omega_1, \omega_2)$ corresponding to Fig. 5.

the purely homogeneous case, one can observe coherent modes of the ground states as shown in this figure.

Figure 8 represents the pure inhomogeneous case, where we can rewrite the response function as

$$R^{(5)}(T_2, T_1) = \int d\omega_1 [A_1 f(\omega_1; B_1, C_1) + A_2 f(\omega_1; B_2, C_2)] \\ \times \{ \cos[\omega_1(T_1 - T_2)] + \cos[\omega_1 T_1] \\ - \cos[\omega_1(T_1 + T_2)] \\ - \cos[\omega_1(T_1 + 2T_2)] \}. \quad (5.14)$$

Thus the response function consists of functions of the form $f(T_1 - T_2)$, $g(T_1 + T_2)$, $j(T_1 + T_2)$, and $k(T_1)$. Since we performed the Fourier transformation over T_1 , $T_2 \geq 0$, the contributions of $f(T_1 - T_2)$ and $k(T_1)$ are large compared with the contribution from $g(T_1 + T_2)$ and $j(T_1 + 2T_2)$ and show maxima along the lines $\omega_1 = -\omega_2$ and $\omega_2 = 0$. The distribution of the ground state mode frequency can be observed on these lines as the peaks at

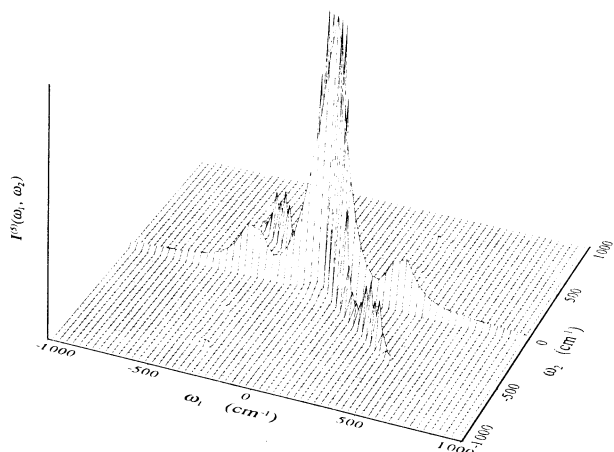


FIG. 8. The frequency domain 2D signal $I^{(5)}(\omega_1, \omega_2)$ corresponding to Fig. 6.

$(\omega_1, \omega_2) = (\pm \omega_b, 0)$ and $(\omega_1, \omega_2) = \pm(\omega_b, -\omega_b)$. The functions $g(T_1 + T_2)$ and $j(T_1 + 2T_2)$ also show small peaks at $(\omega_1, \omega_2) = \pm(\omega_b, \omega_b)$ and $(\omega_1, \omega_2) = \pm(\omega_b, 2\omega_b)$, however, the contribution from ω_a cannot be distinguished from the central peak.

In summary, the two models, which have an identical 1D (birefringence) spectrum clearly show very different 2D spectra. Realistic situations of the liquid spectral density are expected to be intermediate between these purely homogeneous and inhomogeneous cases. $J(\omega; \Gamma)$ and $S(\Gamma)$ may thus be probed separately by performing higher order measurements, in addition to the optical Kerr experiment.

VI. DISCUSSION

In this paper, we calculated the nuclear response function for an off-resonant experiment employing optical pulses, by starting with the effective Hamiltonian Eq. (2.5), and showed how the multidimensional spectrum can be used to distinguish between homogeneous and inhomogeneous line broadening mechanisms. We can derive the same result from the expression of $2N + 1$ th order non-Condon response functions for a displaced two-level oscillator system (see Appendix C). This model can be used to describe electronically resonant as well as off-resonant measurements, and in the off resonance limit it coincides with our effective Hamiltonian approach.

We assume that the material part of Hamiltonian Eq. (2.1) has the form

$$H_0 = |g\rangle H_g(\mathbf{p}, \mathbf{q}) \langle g| + |e\rangle [H_e(\mathbf{p}, \mathbf{q}) + \omega_{eg}] \langle e| \\ + \sum_s \sum_k \left[\frac{(p_k^s)^2}{2m_k^s} + \frac{m_k^s (\omega_k^s)^2}{2} \left(x_k^s - \frac{c_k^s q_s}{m_k^s (\omega_k^s)^2} \right)^2 \right]. \quad (6.1)$$

where $H_g(\mathbf{p}, \mathbf{q})$ is given by Eq. (4.1) and

$$H_e(\mathbf{p}, \mathbf{q}) = \sum_s \left(\frac{p_s^2}{2m_s} + \frac{1}{2} m_s \omega_s^2 (q_s - D_s)^2 \right). \quad (6.2)$$

The constant D_s represents the displacement of the s th oscillator mode. The dipole interaction between the system and the electric field $E(\mathbf{r}, t)$ is

$$V = |g\rangle \mu(\mathbf{q}) \langle e| + |e\rangle \mu(\mathbf{q}) \langle g|, \quad (6.3)$$

where the transition dipole matrix element is a function of the nuclear coordinates and denoted by $\mu(\mathbf{q})$ (non-Condon dipole interaction). We take it to be in the form,

$$\mu(\mathbf{q}) = \mu_0 \exp\left(\sum_s A_s b q_s \right), \quad (6.4)$$

By expanding the density matrix in powers of the field amplitudes, the polarization to $2N + 1$ th order can be expressed as

$$\begin{aligned}
P^{(2N+1)}(t) &\equiv \text{tr}\{V\rho^{(2N+1)}(t)\} \\
&= \int_0^\infty dt_{2N+1} E_T(\mathbf{r}, t-t_{2N+1}) \\
&\quad \times \left[\prod_{j=1}^N \int_0^\infty dt_{2j} \int_0^\infty dt_{2j-1} \right. \\
&\quad \times E_j\left(\mathbf{r}, t - \sum_{k=2j}^{2N+1} t_k\right) E_j\left(\mathbf{r}, t - \sum_{k=2j-1}^{2N+1} t_k\right) \left. \right] \\
&\quad \times R^{(2N+1)}(t). \tag{6.5}
\end{aligned}$$

Here the $2N+1$ th order non-Condon response function is given by

$$\begin{aligned}
R^{(2N+1)}(\mathbf{t}) &= \mu_0^{2N+2} \left(-\frac{i}{\hbar}\right)^{2N+1} \sum_\alpha \int d\Gamma S(\Gamma) \\
&\quad \times \exp[Q_\alpha(\mathbf{t}; \Gamma) + X_\alpha(\mathbf{t}; \Gamma)], \tag{6.6}
\end{aligned}$$

where $Q_\alpha(\mathbf{t}; \Gamma)$ is the Condon contribution of the response function, whereas $X_\alpha(\mathbf{t}; \Gamma)$ is the non-Condon contribution. The sum over α is taken for all possible Liouville paths to $2N+1$ th order. Explicit expressions of $Q_\alpha(\mathbf{t}; \Gamma)$ and $X_\alpha(\mathbf{t}; \Gamma)$ for different Liouville paths are given in Appendix C. The contribution of $Q_\alpha(\mathbf{t}; \Gamma)$ is larger than $X_\alpha(\mathbf{t}; \Gamma)$ in a resonant case, whereas the opposite is true for the off-resonant case. The function $Q_\alpha(\mathbf{t}; \Gamma)$ consists of the function $g_\pm(\mathbf{t}; \Gamma)$, which is a double time integration of $C_\pm(\mathbf{t}; \Gamma)$ plus $\omega_{eg}t$, whereas $X_\alpha(\mathbf{t}; \Gamma)$ consists of $C_\pm(\mathbf{t}; \Gamma)$ itself.

Although the present analysis focused on off-resonant measurements employing optical pulses, this is by no means the only method for obtaining this information. An alternative route will be to use infrared pulses to probe the vibrational transitions directly.⁴⁰ In this case we should replace the $E^2(\mathbf{r}, t)\alpha(\mathbf{q})$ coupling in our effective Hamiltonian by $E(\mathbf{r}, t)\mu(\mathbf{q})$, $\mu(\mathbf{q})$ being the transition dipole moment. We can therefore use the present formation by simply replacing the multitime correlation functions of $\alpha(\mathbf{q})$ by the corresponding correlation functions of $\mu(\mathbf{q})$. By assuming that $\mu(\mathbf{q})$ has an exponential dependence on \mathbf{q} we can then use all the present results. Performing these experiments in the infrared has some advantages since we need lower order nonlinearities (an infrared photon echo is a $P^{(3)}$ process whereas the Raman echo is $P^{(7)}$). On the

other hand, infrared detection and ultrafast technology is less developed than its optical counterpart. Moreover, despite the formal similarity in the description of off-resonant optical and resonant infrared measurements, in practice $\mu(\mathbf{q})$ and $\alpha(\mathbf{q})$ may couple to different types of motions since the dependence of $\alpha(\mathbf{q})$ on \mathbf{q} is not only through $\mu(\mathbf{q})$ but also through the excited state energies. A recent comparison of correlation functions of μ and α in liquid water and water clusters shows major differences.³² Thus the two modes of performing the experiment are complementary.

ACKNOWLEDGMENTS

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APPENDIX A: DERIVATION OF THE EFFECTIVE HAMILTONIAN FOR A TWO-ELECTRIC LEVEL SYSTEM

In this Appendix, we demonstrate how one can deduce the effective Hamiltonian Eq. (2.5) starting from a displaced oscillator model. Denoting the ground and the first excited electronic levels of the system by $|g\rangle$ and $|e\rangle$, respectively, we can write the Hamiltonian in the form,

$$H = H_0 - E(\mathbf{r}, t)V. \tag{A1}$$

Here

$$H_0 = |g\rangle H_g(\mathbf{p}, \mathbf{q}) \langle g| + |e\rangle [H_e(\mathbf{p}, \mathbf{q}) + \omega_{eg}] \langle e|, \tag{A2}$$

and $H_g(\mathbf{p}, \mathbf{q})$ and $H_e(\mathbf{p}, \mathbf{q})$ are the adiabatic Hamiltonians, where \mathbf{p} and \mathbf{q} represent the coordinates and momenta of the nuclear degrees of freedom. The interaction between the system and the electric field $E(\mathbf{r}, t)$ is assumed to be of a dipole form,

$$V = |g\rangle \mu(\mathbf{q}) \langle e| + |e\rangle \mu(\mathbf{q}) \langle g|, \tag{A3}$$

where the transition dipole matrix element is a function of the nuclear coordinates and denoted by $\mu(\mathbf{q})$ (non-Condon dipole interaction).

By expanding the density matrix in powers of the field amplitudes, the polarization to $2N+1$ th order can be expressed as

$$\begin{aligned}
P^{(2N+1)}(t) &\equiv \text{tr}\{V\rho^{(2N+1)}(t)\} \\
&= \left(-\frac{i}{\hbar}\right)^{2N+1} \int_0^\infty dt_{2N+1} E_T(\mathbf{r}, t-t_{2N+1}) \left[\prod_{j=1}^N \int_0^\infty dt_{2j} \int_0^\infty dt_{2j-1} E_j\left(\mathbf{r}, t - \sum_{k=2j}^{2N+1} t_k\right) \right. \\
&\quad \times E_j\left(\mathbf{r}, t - \sum_{k=2j-1}^{2N+1} t_k\right) \left. \right] \text{tr} \left\{ V \left[\prod_{j=1}^{2N+1} \exp\left(-\frac{i}{\hbar} H^\times t_j\right) V^\times \right] \rho_g \right\}, \tag{A4}
\end{aligned}$$

where we introduced the superoperator notation $A^\times B^\times \equiv AB - BA$ and $\exp[iA^\times]B \equiv \exp[iA]B \exp[-iA]$, for any operators A and B . Since each V^\times is a commutator that can act either from the left or from the right, the above expression contains 2^{2N+1} terms. Each term corresponds to a distinct Liouville space path. The electronic state of the system is initially $|g\rangle\langle g|$ for all paths. During the odd time periods t_{2k+1} the system is in an electronic coherence $|e\rangle\langle g|$ or $|g\rangle\langle e|$, whereas during the even time periods t_{2k} it is in an electronic population $|g\rangle\langle g|$ or $|e\rangle\langle e|$, where $1 \leq k \leq N$. For off-resonant excitation, Ω_j and $\Omega'_j \ll \omega_{eg}$, the pulses cannot create real electronic excitation $|e\rangle\langle e|$ and all paths containing at least one $|e\rangle\langle e|$ period can be neglected. The remaining terms represent Raman processes whose Liouville paths only involve $|g\rangle\langle e|$, $|e\rangle\langle g|$ and $|g\rangle\langle g|$. For off-resonance laser fields, we can further make the following approximation for the contribution of the optical coherence periods $|e\rangle\langle g|$ and $|g\rangle\langle e|$:⁷

$$\begin{aligned} & \left(-\frac{i}{\hbar}\right)^2 \int_0^\infty dt_{2j-1} E_j(\mathbf{r}, \tau) E_j^*(\mathbf{r}, \tau - t_{2j-1}) \langle g|V|e\rangle \\ & \times \left\langle e \left| \exp\left(\pm \frac{i}{\hbar} H_0 t_{2j-1}\right) \right| e \right\rangle \langle e|V|g\rangle \\ & \approx \mp \frac{2i}{\hbar} |E_j(\tau)|^2 \alpha_j(\mathbf{q}) [2 \cos(\Delta\Omega_j \tau - \Delta\mathbf{k}_j \mathbf{r}) + 1], \end{aligned} \quad (\text{A5})$$

where $\Delta\mathbf{k}_j \equiv \mathbf{k}_j - \mathbf{k}'_j$, $\Delta\Omega_j \equiv \Omega_j - \Omega'_j$ and

$$\alpha_j(\mathbf{q}) \equiv \frac{\mu^2(\mathbf{q})}{\hbar} \left(\frac{1}{\omega_{eg} + \Omega_j} + \frac{1}{\omega_{eg} - \Omega_j} \right), \quad (\text{A6})$$

is the linear polarizability tensor. For clarity we hereafter assume that the polarizability is isotropic, and do not use an explicit tensor notation; this can be incorporated with no major difficulty.²⁰

For off-resonant excitation, the $2N+1$ th polarization is then expressed as

$$\begin{aligned} P^{(2N+1)}(t) &= 2^{N+1} E_T(t) \exp(i\Omega_T t - i\mathbf{k}_T \mathbf{r}) \\ & \times \left\{ \prod_{j=1}^N \int_0^\infty d\tau_j E_j^2 \left(t - \sum_{k=j}^N \tau_k \right) \right. \\ & \times \left. \left[\chi \cos \left(\Delta\Omega_j \left(t - \sum_{k=j}^N \tau_k \right) - \Delta\mathbf{k}_j \mathbf{r} \right) + 1 \right] \right\} \\ & \times R^{(2N+1)}(\{\tau_j\}), \end{aligned} \quad (\text{A7})$$

where the $2N+1$ th order response function is now given by

$$\begin{aligned} R^{(2N+1)}(\{\tau_j\}) &\equiv \left(\frac{i}{\hbar}\right)^N \text{tr} \left\{ \alpha(\mathbf{q}) \left[\prod_{j=1}^N \right. \right. \\ & \left. \left. \times \exp\left(-\frac{i}{\hbar} H_g^\times \tau_j\right) \alpha^\times(\mathbf{q}) \right] \rho_g \right\}. \end{aligned} \quad (\text{A8})$$

Here $\alpha^\times A \equiv [\alpha, A]$ represents the commutator with the electronic polarizability, and we have neglected the weak dependence of α_j on the frequency Ω_j and assumed $\alpha_j(\mathbf{q}) = \alpha(\mathbf{q})$. This response function depends only on ground electronic state dynamics and is equivalent to considering the following effective ground state nuclear Hamiltonian,⁷ where the electronic excited state has been eliminated,

$$H = H_g(\mathbf{p}, \mathbf{q}) - E^2(\mathbf{r}, t) \alpha(\mathbf{q}). \quad (\text{A9})$$

APPENDIX B: PHASE SPACE DISTRIBUTION FUNCTIONS FOR 2Mth ORDER OPTICAL PROCESSES

We can calculate the density matrix elements relevant for the $2N$ th order off-resonant optical processes by performing a path integral. Since the calculation is similar to Ref. 28, we only present the results. In the Wigner representation defined by

$$W^{(2N)}(p, q, t) \equiv \frac{1}{2\pi\hbar} \int dx e^{-ipx/\hbar} \rho^{(2N)}\left(q + \frac{x}{2}, q - \frac{x}{2}, t\right), \quad (\text{B1})$$

the nuclear wave packet corresponding to a given Liouville space path is given by

$$\begin{aligned} W^{(2N)}(p, q; t) &= \frac{2^N}{\hbar^{N-1}} \left\{ \left(\prod_{j=1}^{N-1} \int_0^\infty d\tau_j \right) \left| E_j \left(t - \sum_{k=j}^{N-1} \tau_k \right) \right|^2 \left[\chi \cos \left(\Delta\Omega_j \left(t - \sum_{k=j}^{N-1} \tau_k \right) - \Delta\mathbf{k}_j \mathbf{r} \right) + 1 \right] \right\} \\ & \times \left[\lim_{a \rightarrow 0} \frac{1}{\hbar^{N-1}} \sum_{\epsilon_1 = \pm} \sum_{\epsilon_2 = \pm} \cdots \sum_{\epsilon_N = \pm} \epsilon_1 \epsilon_2 \cdots \epsilon_N \hat{\alpha}_1 \hat{\alpha}_2 \cdots \hat{\alpha}_{N+1} G^{(2N)}(p, q; \mathbf{a}; \{\tau_j\}) \right]. \end{aligned} \quad (\text{B2})$$

Here the generating function for the phase space wave packet is given by

$$\begin{aligned} G^{(2N)}(p, q; \mathbf{a}; \{\tau_j\}) &= \frac{1}{A} \exp \left[-\frac{1}{2\langle q^2 \rangle} (q - \bar{q}(t, \mathbf{a}))^2 \right. \\ & \left. - \frac{1}{2\langle p^2 \rangle} (p - \bar{p}(t, \mathbf{a}))^2 \right] F^{(2N)}(\mathbf{a}; \{\tau_j\}), \end{aligned} \quad (\text{B3})$$

where

$$\bar{q}(t, \mathbf{a}) = \sum_{j=1}^N a_j C_{\epsilon_j} \left(t - \sum_{k=1}^j \tau_k \right), \quad (\text{B4})$$

$$\begin{aligned} \bar{p}(t, \mathbf{a}) &= M \sum_{j=1}^N a_j \dot{C}_{\epsilon_j} \left(t - \sum_{k=1}^j \tau_k \right), \\ \langle q^2 \rangle &\equiv C'(0), \quad \langle p^2 \rangle \equiv -M^2 \dot{C}'(0), \end{aligned} \quad (\text{B5})$$

and

$$A \equiv 2\pi \sqrt{\langle p^2 \rangle \langle q^2 \rangle}. \quad (\text{B6})$$

APPENDIX C: CONNECTION WITH ELECTRONICALLY RESONANT NONLINEAR RESPONSE FUNCTIONS

In this paper, we calculated the off-resonant non-Condon response function by employing the effective Hamiltonian Eq. (2.5). This derivation, does not require specifying a potential surface of the excited state. We can obtain the same results from a general expressions of the non-Condon response function for a displaced harmonic oscillators system, which applies to resonant as well as off-resonant spectroscopy.

We consider the system described by the Hamiltonian Eq. (6.1) with the dipole interaction Eq. (6.3) and calculate the $2N+1$ th order response function

$$R^{(2N+1)}(\mathbf{t}) \equiv \left(-\frac{i}{\hbar} \right)^{2N+1} \times \text{tr} \left\{ V \left[\prod_{j=1}^{2N+1} \exp \left(-\frac{i}{\hbar} H^\times t_j \right) V^\times \right] \rho_g \right\}, \quad (\text{C1})$$

The response function contains 2^{2N+1} terms denoted *Liouville space paths*. They come from taking $2N+1$ commutators with the dipole operator V in the evaluation of the density matrix. The electronic state of the system is initially $|g\rangle\langle g|$ for all paths. In each path the system undergoes $2N+1$ evolution periods denoted chronologically by $t_1, t_2, \dots, t_{2N+1}$. The paths differ by which electronic density matrix element exists in each of these periods. Mathematically, we can represent the path by $2N+1$ indices ϵ_j , which are chosen as follows: When the density matrix during the j th period t_j is in the state ρ_{gg} , ρ_{ee} , ρ_{eg} , and ρ_{ge} ,

TABLE I. Possible Liouville paths and the corresponding auxiliary parameters ϵ_j for calculating the response function to fifth order. In the table (gg), (ee), (eg), and (ge) represent the density matrix elements ρ_{gg} , ρ_{ee} , ρ_{eg} , and ρ_{ge} , respectively. The complex conjugate paths to 1–16, which can be obtained by setting $\epsilon_5 = -(ge)$, are not shown. The system is initially in the ground state (gg) and we set $\epsilon_0 = -$.

α	ϵ_1	ϵ_2	ϵ_3	ϵ_4	ϵ_5
1	+(eg)	-(gg)	+(eg)	-(gg)	+(eg)
2	-(ge)	-(gg)	+(eg)	-(gg)	+(eg)
3	+(eg)	-(gg)	-(ge)	-(gg)	+(eg)
4	-(ge)	-(gg)	-(ge)	-(gg)	+(eg)
5	+(eg)	-(gg)	-(ge)	+(ee)	+(eg)
6	-(ge)	-(gg)	-(ge)	+(ee)	+(eg)
7	+(eg)	-(gg)	+(eg)	+(ee)	+(eg)
8	-(ge)	-(gg)	+(eg)	+(ee)	+(eg)
9	+(eg)	+(ee)	+(eg)	-(gg)	+(eg)
10	-(ge)	+(ee)	+(eg)	-(gg)	+(eg)
11	+(eg)	+(ee)	-(ge)	-(gg)	+(eg)
12	-(ge)	+(ee)	-(ge)	-(gg)	+(eg)
13	+(eg)	+(ee)	-(ge)	+(ee)	+(eg)
14	-(ge)	+(ee)	-(ge)	+(ee)	+(eg)
15	+(eg)	+(ee)	+(eg)	+(ee)	+(eg)
16	-(ge)	+(ee)	+(eg)	+(ee)	+(eg)

we have $\epsilon_j = -1, +1, +1$, and -1 respectively. We label a combination of ϵ_j by α (i.e., $\alpha \equiv \{\epsilon_j\}$). As an example, we present the Liouville paths of the fifth order optical processes and corresponding sign parameters in Table I.

For a non-Condon dipole moment Eq. (6.4), the $2N+1$ th order non-Condon response function is given by²⁸

$$R^{(2N+1)}(\mathbf{t}) = \mu_0^{2N+2} \left(-\frac{i}{\hbar} \right)^{2N+1} \prod_s \sum_\alpha \times \exp[Q_\alpha^s(\mathbf{t}) + X_\alpha^s(\mathbf{t})] + \text{c.c.}, \quad (\text{C2})$$

where $Q_\alpha^s(\mathbf{t})$ and $X_\alpha^s(\mathbf{t})$ are the Condon and non-Condon parts of the s th mode response functions written as

$$Q_\alpha^s(\mathbf{t}) = -i\omega_{eg}^s \sum_{j=1}^{N+1} \epsilon_{2j-1} t_{2j-1} - \sum_{j=1}^{N+1} g_{\epsilon_{2j-1}\epsilon_{2j-2}}^s(t_{2j-1}) - \sum_{j=k+1}^{N+1} \sum_{k=1}^N \epsilon_{2j-1}\epsilon_{2k-1} \left[g_{\epsilon_{2k}\epsilon_{2k-1}}^s \left(\sum_{l=2k}^{2j-2} t_l \right) - g_{\epsilon_{2k}\epsilon_{2k-1}}^s \left(\sum_{l=2k}^{2j-1} t_l \right) - g_{\epsilon_{2k-1}\epsilon_{2k-2}}^s \left(\sum_{l=2k-1}^{2j-2} t_l \right) + g_{\epsilon_{2k-1}\epsilon_{2k-2}}^s \left(\sum_{l=2k-1}^{2j-1} t_l \right) \right] \quad (\text{C3})$$

and

$$X_\alpha^s(\mathbf{t}) = \sum_{k=1}^{2N+2} b \langle \bar{q}_k^s(\mathbf{t}) \rangle_\alpha + \sum_{k=m+1}^{2N+2} \sum_{m=1}^{2N+1} b^2 C_{\epsilon_m \epsilon_{m-1}}^s \left(\sum_{l=m}^{k-1} t_l \right) + \sum_{k=1}^{2N+2} \frac{b^2}{2} C^{rs}(0), \quad (\text{C4})$$

where

$$\langle \bar{q}_k^s(\mathbf{t}) \rangle_\alpha = -i\xi_s \left[\sum_{m=0}^{k>2m+1} \epsilon_{2m+1} h_{\epsilon_{2m}\epsilon_{2m+1}}^s \left(\sum_{l=2m+1}^{k-1} t_l \right) - \sum_{m=1}^{k>2m} \epsilon_{2m-1} h_{\epsilon_{2m}\epsilon_{2m-1}}^s \left(\sum_{l=2m}^{k-1} t_l \right) - \sum_{2m+1>k}^{m=N} \epsilon_{2m+1} h_{\epsilon_k \epsilon_{k-1}}^s \left(\sum_{l=k}^{2m} t_l \right) + \sum_{2m>k}^{m=N+1} \epsilon_{2m-1} h_{\epsilon_k \epsilon_{k-1}}^s \left(\sum_{l=k}^{2m-1} t_l \right) \right]. \quad (\text{C5})$$

In the above we set $\omega_{eg}^s = \omega_{eg} + m_s D_s^2 \omega_s^2 / 2\hbar$ and $\xi_s \equiv m_s D_s \omega_s^2 / \hbar$. The correlation function for the s th mode $C_\pm^s(t)$ is defined by Eq. (4.5) with Eq. (4.8) and $C^{rs}(t)$ is the real part of $C_\pm^s(t)$. Using this we defined the auxiliary functions

$$h_{\pm}^s(t) \equiv \xi_s \int_0^t dt' C_{\pm}^s(t'), \quad (C6)$$

and

$$g_{\pm}^s(t) \equiv \xi_s^2 \int_0^t dt' \int_0^{t'} dt'' C_{\pm}^s(t''). \quad (C7)$$

The summations \sum_{α} in Eq. (C2) represents sum for possible sign $\epsilon_1, \epsilon_2, \dots, \epsilon_{2N} = \pm$, and $\epsilon_{2N+1} = +$, which yields the necessary 2^{2N} Liouville space paths. The other 2^{2N} Liouville space paths are simply their complex conjugate and can be obtained by choosing $\epsilon_{2N+1} = -$.

We can introduce inhomogeneous broadening by the following average:

$$R^{(2N+1)}(\mathbf{t}) = \mu_0^{2N+2} \left(-\frac{i}{\hbar} \right)^{2N+1} \sum_{\alpha} \int d\Gamma S(\Gamma) \exp[Q_{\alpha}(\mathbf{t}; \Gamma) + X_{\alpha}(b; \mathbf{t}; \Gamma)] + \text{c.c.}, \quad (C8)$$

where $S(\Gamma)$ is the distribution function of the set of parameters $\Gamma = \{\eta_s, \omega_s, \gamma_s\}$ and we replaced

$$\sum_s Q_{\alpha}^s(\mathbf{t}) \rightarrow Q_{\alpha}(\mathbf{t}; \Gamma), \quad \sum_s X_{\alpha}^s(\mathbf{t}) \rightarrow X_{\alpha}(\mathbf{t}; \Gamma). \quad (C9)$$

As an example, we present the fifth order of $Q_{\alpha}(\mathbf{t}; \Gamma)$ and $X_{\alpha}(\mathbf{t}; \Gamma)$;

$$\begin{aligned} Q_{\alpha}(\mathbf{t}; \Gamma) = & -i\omega'_{eg}(\epsilon_1 t_1 + \epsilon_3 t_3 + \epsilon_5 t_5) - g_{\epsilon_1 \epsilon_0}(t_1; \Gamma) - g_{\epsilon_3 \epsilon_2}(t_3; \Gamma) - g_{\epsilon_5 \epsilon_4}(t_5; \Gamma) - \epsilon_3 \epsilon_1 [g_{\epsilon_2 \epsilon_1}(t_2; \Gamma) - g_{\epsilon_2 \epsilon_1}(t_2 + t_3; \Gamma) \\ & - g_{\epsilon_1 \epsilon_0}(t_1 + t_2; \Gamma) + g_{\epsilon_1 \epsilon_0}(t_1 + t_2 + t_3; \Gamma)] - \epsilon_5 \epsilon_1 [g_{\epsilon_3 \epsilon_1}(t_2 + t_3 + t_4; \Gamma) - g_{\epsilon_2 \epsilon_1}(t_2 + t_3 + t_4 + t_5; \Gamma) \\ & - g_{\epsilon_1 \epsilon_0}(t_1 + t_2 + t_3 + t_4; \Gamma) + g_{\epsilon_1 \epsilon_0}(t_1 + t_2 + t_3 + t_4 + t_5; \Gamma)] - \epsilon_5 \epsilon_3 [g_{\epsilon_4 \epsilon_3}(t_4; \Gamma) - g_{\epsilon_4 \epsilon_3}(t_4 + t_5; \Gamma) \\ & - g_{\epsilon_3 \epsilon_2}(t_3 + t_4; \Gamma) + g_{\epsilon_3 \epsilon_2}(t_3 + t_4 + t_5; \Gamma)], \end{aligned} \quad (C10)$$

and

$$\begin{aligned} X_{\alpha}(\mathbf{t}; \Gamma) = & b \sum_{k=1}^6 \langle \bar{q}_k(\mathbf{t}; \Gamma) \rangle_{\alpha} + \sum_{k=1}^6 \frac{b^2}{2} C'(0; \Gamma) + b^2 [C_{\epsilon_1 \epsilon_0}(t_1; \Gamma) + C_{\epsilon_1 \epsilon_0}(t_1 + t_2; \Gamma) + C_{\epsilon_1 \epsilon_0}(t_1 + t_2 + t_3; \Gamma) \\ & + C_{\epsilon_1 \epsilon_0}(t_1 + t_2 + t_3 + t_4; \Gamma) + C_{\epsilon_1 \epsilon_0}(t_1 + t_2 + t_3 + t_4 + t_5; \Gamma) + C_{\epsilon_2 \epsilon_1}(t_2; \Gamma) + C_{\epsilon_2 \epsilon_1}(t_2 + t_3; \Gamma) \\ & + C_{\epsilon_2 \epsilon_1}(t_2 + t_3 + t_4; \Gamma) + C_{\epsilon_2 \epsilon_1}(t_2 + t_3 + t_4 + t_5; \Gamma) + C_{\epsilon_3 \epsilon_2}(t_3; \Gamma) + C_{\epsilon_3 \epsilon_2}(t_3 + t_4; \Gamma) + C_{\epsilon_3 \epsilon_2}(t_3 + t_4 + t_5; \Gamma) \\ & + C_{\epsilon_4 \epsilon_3}(t_4; \Gamma) + C_{\epsilon_4 \epsilon_3}(t_4 + t_5; \Gamma) + C_{\epsilon_5 \epsilon_4}(t_5; \Gamma)], \end{aligned} \quad (C11)$$

where

$$\begin{aligned} \langle \bar{q}_1(\mathbf{t}; \Gamma) \rangle_{\alpha} = & -i[\epsilon_1 h_{\epsilon_0 \epsilon_1}(t_1; \Gamma) + \epsilon_3 h_{\epsilon_0 \epsilon_1}(t_1 + t_2 + t_3; \Gamma) + \epsilon_5 h_{\epsilon_0 \epsilon_1}(t_1 + t_2 + t_3 + t_4 + t_5; \Gamma) - \epsilon_3 h_{\epsilon_0 \epsilon_1}(t_1 + t_2; \Gamma) \\ & - \epsilon_5 h_{\epsilon_0 \epsilon_1}(t_1 + t_2 + t_3 + t_4; \Gamma)], \\ \langle \bar{q}_2(\mathbf{t}; \Gamma) \rangle_{\alpha} = & -i[\epsilon_1 h_{\epsilon_0 \epsilon_1}(t_1; \Gamma) + \epsilon_3 h_{\epsilon_1 \epsilon_2}(t_2 + t_3; \Gamma) + \epsilon_5 h_{\epsilon_1 \epsilon_2}(t_2 + t_3 + t_4 + t_5; \Gamma) - \epsilon_3 h_{\epsilon_1 \epsilon_2}(t_2; \Gamma) - \epsilon_5 h_{\epsilon_1 \epsilon_2}(t_2 + t_3 + t_4; \Gamma)], \\ \langle \bar{q}_3(\mathbf{t}; \Gamma) \rangle_{\alpha} = & -i[\epsilon_1 h_{\epsilon_0 \epsilon_1}(t_1 + t_2; \Gamma) - \epsilon_1 h_{\epsilon_1 \epsilon_2}(t_2; \Gamma) - \epsilon_5 h_{\epsilon_2 \epsilon_3}(t_3 + t_4; \Gamma) + \epsilon_3 h_{\epsilon_2 \epsilon_3}(t_3; \Gamma) + \epsilon_5 h_{\epsilon_2 \epsilon_3}(t_3 + t_4 + t_5; \Gamma)], \\ \langle \bar{q}_4(\mathbf{t}; \Gamma) \rangle_{\alpha} = & -i[\epsilon_1 h_{\epsilon_0 \epsilon_1}(t_1 + t_2 + t_3; \Gamma) + \epsilon_3 h_{\epsilon_2 \epsilon_3}(t_3; \Gamma) - \epsilon_1 h_{\epsilon_1 \epsilon_2}(t_2 + t_3; \Gamma) - \epsilon_5 h_{\epsilon_3 \epsilon_4}(t_4; \Gamma) + \epsilon_5 h_{\epsilon_3 \epsilon_4}(t_4 + t_5; \Gamma)], \\ \langle \bar{q}_5^s(\mathbf{t}; \Gamma) \rangle_{\alpha} = & -i[\epsilon_1 h_{\epsilon_0 \epsilon_1}(t_1 + t_2 + t_3 + t_4; \Gamma) + \epsilon_3 h_{\epsilon_2 \epsilon_3}(t_3 + t_4; \Gamma) - \epsilon_1 h_{\epsilon_1 \epsilon_2}(t_2 + t_3 + t_4; \Gamma) - \epsilon_3 h_{\epsilon_3 \epsilon_4}(t_4; \Gamma) + \epsilon_5 h_{\epsilon_4 \epsilon_5}(t_5; \Gamma)], \\ \langle \bar{q}_6(\mathbf{t}; \Gamma) \rangle_{\alpha} = & -i[\epsilon_1 h_{\epsilon_0 \epsilon_1}(t_1 + t_2 + t_3 + t_4 + t_5; \Gamma) + \epsilon_3 h_{\epsilon_2 \epsilon_3}(t_3 + t_4 + t_5; \Gamma) + \epsilon_5 h_{\epsilon_4 \epsilon_5}(t_5; \Gamma) - \epsilon_1 h_{\epsilon_1 \epsilon_2}(t_2 + t_3 + t_4 + t_5; \Gamma) \\ & - \epsilon_3 h_{\epsilon_3 \epsilon_4}(t_4 + t_5; \Gamma)]. \end{aligned} \quad (C12)$$

For off-resonance experiments, we can perform the time integrations over odd period [see Eq. (A5)] and the result can be obtained by setting $t_{2j+1} = 0$ in the above expression. All contributions of the Condon part $Q_{\alpha}(\mathbf{t}; \Gamma)$ for different Liouville path α then vanish and we have only non-Condon contribution;

$$X_\alpha(\mathbf{t}; \Gamma) = b \sum_{k=1}^6 \langle \bar{q}_k(\mathbf{t}; \Gamma) \rangle_\alpha + 6b^2 C'(0; \Gamma) + 2b^2 [C_{\epsilon_1 \epsilon_0}(t_2; \Gamma) + C_{\epsilon_2 \epsilon_1}(t_2; \Gamma) + C_{\epsilon_1 \epsilon_0}(t_2 + t_4; \Gamma) + C_{\epsilon_2 \epsilon_1}(t_2 + t_4; \Gamma) + C_{\epsilon_3 \epsilon_2}(t_4; \Gamma) + C_{\epsilon_4 \epsilon_3}(t_4; \Gamma)], \quad (\text{C13})$$

where

$$\begin{cases} \langle \bar{q}_1(\mathbf{t}; \Gamma) \rangle_\alpha = \langle \bar{q}_2(\mathbf{t}; \Gamma) \rangle_\alpha = 0, \\ \langle \bar{q}_3(\mathbf{t}; \Gamma) \rangle_\alpha = \langle \bar{q}_4(\mathbf{t}; \Gamma) \rangle_\alpha = -i[\epsilon_1 h_{\epsilon_0 \epsilon_1}(t_2) - \epsilon_1 h_{\epsilon_1 \epsilon_2}(t_2)] \\ \langle \bar{q}_5(\mathbf{t}; \Gamma) \rangle_\alpha = \langle \bar{q}_6(\mathbf{t}; \Gamma) \rangle_\alpha = -i[\epsilon_1 h_{\epsilon_0 \epsilon_1}(t_2 + t_4; \Gamma) - \epsilon_1 h_{\epsilon_1 \epsilon_2}(t_2 + t_4; \Gamma) + \epsilon_3 h_{\epsilon_2 \epsilon_3}(t_4; \Gamma) - \epsilon_3 h_{\epsilon_3 \epsilon_4}(t_4; \Gamma)]. \end{cases} \quad (\text{C14})$$

For the Liouville paths which involves ee , the terms in Eq. (C14) becomes real functions. For example, for the path $\alpha=9$ in Table I, we have $\langle \bar{q}_3(\mathbf{t}; \Gamma) \rangle_9 = \langle \bar{q}_4(\mathbf{t}; \Gamma) \rangle_9 = -\text{Re}(h_-(t_2))$. These functions are positive in time and thus the contribution of the response function from the Liouville paths $\alpha=5-16$, which involve the excitation processes ee are smaller than those from $\alpha=1-4$. Thus by setting $\epsilon_2, \epsilon_4 = -$, the phase of the non-Condon response function reduces to

$$X_\alpha(\mathbf{t}; \Gamma) = 6b^2 C'(0; \Gamma) + 4b^2 [C_{-\epsilon_1}(t_2; \Gamma) + C_{-\epsilon_1}(t_2 + t_4; \Gamma) + C_{-\epsilon_3}(t_4; \Gamma)]. \quad (\text{C15})$$

The response function is then given by

$$R^{(5)}(\mathbf{t}; \Gamma) = -\frac{\alpha_0^3}{\hbar^2} \sum_{\epsilon_1 = \pm} \sum_{\epsilon_3 = \pm} \epsilon_1 \epsilon_3 \exp\left\{ \frac{3a^2}{2} C'(0; \Gamma) + a^2 [C_{-\epsilon_1}(\tau_1; \Gamma) + C_{-\epsilon_1}(\tau_1 + \tau_2; \Gamma) + C_{-\epsilon_3}(\tau_2; \Gamma)] \right\}, \quad (\text{C16})$$

where we set $a=2b$, $\tau_1=t_2$, and $\tau_2=t_4$. The Liouville paths are replaced by all possible sets of ϵ_j , and the sum over α is replaced by these sum. The sign factor $\epsilon_1 \epsilon_3$ arises from the time integration Eq. (A5). This result is identical to Eq. (4.15).

APPENDIX D: THE SEVENTH ORDER RESPONSE FUNCTION

From Eq. (2.6), the seventh order response function is expressed as

$$P^{(7)}(t) = 2^4 \int_0^\infty d\tau_3 \int_0^\infty d\tau_2 \int_0^\infty d\tau_1 E_T(t) E_3^2(t-\tau_3) E_2^2(t-\tau_3-\tau_2) E_1^2(t-\tau_3-\tau_2-\tau_1) \exp(i\Omega_T t - i\mathbf{k}_T \mathbf{r}) \times [\cos(\Delta\Omega_3(t-\tau_3) - \Delta\mathbf{k}_3 \mathbf{r}) + 1] [\cos(\Delta\Omega_2(t-\tau_3-\tau_2) - \Delta\mathbf{k}_2 \mathbf{r}) + 1] \times [\cos(\Delta\Omega_1(t-\tau_3-\tau_2-\tau_1) - \Delta\mathbf{k}_1 \mathbf{r}) + 1] R^{(7)}(\tau_3, \tau_2, \tau_1), \quad (\text{D1})$$

where

$$R^{(7)}(\tau_3, \tau_2, \tau_1) = -\frac{i}{\hbar^3} \langle [[[[\alpha(t_4), \alpha(t_3)], \alpha(t_2)], \alpha(t_1)] \rho_g \rangle. \quad (\text{D2})$$

Using the generating function, the response function is written as

$$R^{(7)}(\tau_3, \tau_2, \tau_1) = \lim_{a \rightarrow 0} \frac{-i}{\hbar^3} \sum_{\epsilon_1 = \pm} \sum_{\epsilon_2 = \pm} \sum_{\epsilon_3 = \pm} \epsilon_1 \epsilon_2 \epsilon_3 \hat{\alpha}_1 \hat{\alpha}_2 \hat{\alpha}_3 \hat{\alpha}_4 F^{(7)}(\{a_j\}; \tau_3, \tau_2, \tau_1), \quad (\text{D3})$$

where

$$F^{(7)}(\{a_j\}; \tau_3, \tau_2, \tau_1) = \exp[a_4 a_1 C_{-\epsilon_1}(\tau_3 + \tau_2 + \tau_1) + a_4 a_2 C_{-\epsilon_2}(\tau_3 + \tau_2) + a_4 a_3 C_{-\epsilon_3}(\tau_3) + a_3 a_1 C_{-\epsilon_1}(\tau_2 + \tau_1) + a_3 a_2 C_{-\epsilon_2}(\tau_2) + a_2 a_1 C_{-\epsilon_1}(\tau_1) + \frac{1}{2}(a_1^2 + a_2^2 + a_3^2 + a_4^2) C'(0)]. \quad (\text{D4})$$

Assuming an exponential form for the polarization [Eq. (3.14)], the first two terms in the expansion of the response function can be calculated as

$$\begin{aligned}
R^{(7)}(\tau_3, \tau_2, \tau_1) = & \frac{8}{\hbar^3} \alpha_0^4 a^6 C''(\tau_3) [C''(\tau_2) + C''(\tau_2 + \tau_3)] [C''(\tau_1) + C''(\tau_1 + \tau_2) + C''(\tau_1 + \tau_2 + \tau_3)] + \frac{8}{\hbar^3} \alpha_0^4 a^8 C''(\tau_3) \\
& \times [C''(\tau_1) + C''(\tau_1 + \tau_2) + C''(\tau_1 + \tau_2 + \tau_3)] [C''(\tau_2) + C''(\tau_2 + \tau_3)] [C'(\tau_1) + C'(\tau_1 + \tau_2) \\
& + C'(\tau_1 + \tau_2 + \tau_3) + C'(\tau_2) + C'(\tau_2 + \tau_3) + C'(\tau_3) + 2C'(0)] + \dots
\end{aligned} \quad (D5)$$

By incorporating inhomogeneous broadening, the lowest order response function becomes

$$\begin{aligned}
R^{(7)}(\tau_3, \tau_2, \tau_1) = & \frac{8}{\hbar^3} \alpha_0 a^6 \int d\Gamma_\alpha S(\Gamma_\alpha) C''(\tau_3; \Gamma_\alpha) [C''(\tau_2; \Gamma_\alpha) + C''(\tau_2 + \tau_3; \Gamma_\alpha)] [C''(\tau_1; \Gamma_\alpha) \\
& + C''(\tau_1 + \tau_2; \Gamma_\alpha) + C''(\tau_1 + \tau_2 + \tau_3; \Gamma_\alpha)].
\end{aligned} \quad (D6)$$

The seventh order response function has been studied in connection with the Raman echo,¹³ however, the expression of the response function for the present model does not give a simple echo, since the nuclear timescale is finite, and the model is not identical to a two-level system with a homogeneous and an inhomogeneous broadening mechanism.

APPENDIX E: RESPONSE FUNCTIONS FOR A POLYNOMIAL COORDINATE DEPENDENCE OF THE POLARIZABILITY

We assume a non-Condon electronic polarizability in the form

$$\alpha(q) \approx \sum_{n=0}^{\infty} \frac{1}{n!} \alpha_n q^n. \quad (E1)$$

Using the generating function Eq. (3.9), the lowest two terms in the third order response function are calculated as

$$R^{(3)}(\tau_1) = \frac{2i\alpha_1^2}{\hbar} C''(\tau_1) + \frac{2i\alpha_2^2}{\hbar} C''(\tau_1)C'(\tau_1) + \dots \quad (E2)$$

By using the generating function Eq. (3.12), the fifth order response function are calculated as

$$\begin{aligned}
R^{(5)}(\tau_2, \tau_1) = & \frac{4}{\hbar^2} \alpha_1^2 \alpha_2 C''(\tau_2) [C''(\tau_1) + C''(\tau_1 + \tau_2)] + \frac{2}{\hbar^2} \alpha_1^2 \alpha_4 C''(\tau_2) [C''(\tau_1) + C''(\tau_1 + \tau_2)] C'(0) \\
& + \frac{4}{\hbar^2} \alpha_2^3 C''(\tau_2) [C''(\tau_1)C'(\tau_1 + \tau_2) + C''(\tau_1 + \tau_2)C'(\tau_1)] + \frac{4}{\hbar^2} \alpha_1 \alpha_2 \alpha_3 C''(\tau_2) [C''(\tau_1)C'(\tau_1) \\
& + C''(\tau_1 + \tau_2)C'(\tau_1 + \tau_2) + (C''(\tau_1) + C''(\tau_1 + \tau_2))(C'(\tau_2) + C'(0))] + \dots
\end{aligned} \quad (E3)$$

The expression of the Seventh order response function, calculated from Eq. (D4), is lengthy and hereafter we show each term separately, in various orders in α_j .

(1)

$$\frac{8i\alpha_1^2 \alpha_2^2}{\hbar^3} C''(\tau_3) [C''(\tau_1)C''(\tau_2) + C''(\tau_1 + \tau_2 + \tau_3)C''(\tau_2) + C''(\tau_1)C''(\tau_2 + \tau_3) + C''(\tau_1 + \tau_2)C''(\tau_2 + \tau_3)], \quad (E4)$$

(2)

$$\frac{8i\alpha_3 \alpha_1^3}{\hbar^3} C''(\tau_3) [C''(\tau_1 + \tau_2)C''(\tau_2) + C''(\tau_1 + \tau_2 + \tau_3)C''(\tau_2 + \tau_3)]. \quad (E5)$$

(3)

$$\begin{aligned}
\frac{8i\alpha_2^4}{\hbar^3} C''(\tau_3) [(C''(\tau_1 + \tau_2 + \tau_3)C''(\tau_2) + C''(\tau_1 + \tau_2)C''(\tau_2 + \tau_3))C'(\tau_1) \\
+ C''(\tau_1)C''(\tau_2 + \tau_3)C'(\tau_1 + \tau_2) + C''(\tau_1)C''(\tau_2)C'(\tau_1 + \tau_2 + \tau_3)].
\end{aligned} \quad (E6)$$

(4)

$$\frac{4i\alpha_5 \alpha_1^3}{\hbar^3} C''(\tau_3) (C''(\tau_1 + \tau_2)C''(\tau_2) + C''(\tau_1 + \tau_2 + \tau_3)C''(\tau_2 + \tau_3))C'(0). \quad (E7)$$

(5)

$$\begin{aligned} & \frac{4i\alpha_3^2\alpha_1^2}{\hbar^3} C''(\tau_3) [2C''(\tau_1)C''(\tau_2)C'(\tau_2) + 2C''(\tau_1)C''(\tau_2+\tau_3)C'(\tau_2+\tau_3) + 2(C''(\tau_1+\tau_2+\tau_3)C''(\tau_2) \\ & + C''(\tau_1+\tau_2)C''(\tau_2+\tau_3))C'(\tau_3) + 3(C''(\tau_1+\tau_2)C''(\tau_2) \\ & + C''(\tau_1+\tau_2+\tau_3)C''(\tau_2+\tau_3))C'(0)], \end{aligned} \quad (\text{E8})$$

(6)

$$\begin{aligned} & \frac{8i\alpha_3^2\alpha_1^2}{\hbar^3} C''(\tau_3) \{ [(C''(\tau_1) + C''(\tau_1+\tau_2))C''(\tau_2) + (C''(\tau_1) + C''(\tau_1+\tau_2+\tau_3))C''(\tau_2+\tau_3)]C'(\tau_1) \\ & + [(C''(\tau_1) + C''(\tau_1+\tau_2+\tau_3))C''(\tau_2) + (C''(\tau_1+\tau_2) + C''(\tau_1+\tau_2+\tau_3))C''(\tau_2+\tau_3)]C'(\tau_1+\tau_2) + [(C''(\tau_1+\tau_2) \\ & + C''(\tau_1+\tau_2+\tau_3))C''(\tau_2) + (C''(\tau_1) + C''(\tau_1+\tau_2))C''(\tau_2+\tau_3)]C'(\tau_1+\tau_2+\tau_3) + [C''(\tau_1+\tau_2+\tau_3)C''(\tau_2) \\ & + (C''(\tau_1) + C''(\tau_1+\tau_2) + C''(\tau_1+\tau_2+\tau_3))C''(\tau_2+\tau_3)]C'(\tau_2) + [(C''(\tau_1) + C''(\tau_1+\tau_2) + C''(\tau_1+\tau_2+\tau_3))C''(\tau_2) \\ & + C''(\tau_1+\tau_2)C''(\tau_2+\tau_3)]C'(\tau_2+\tau_3) + [(C''(\tau_1) + C''(\tau_1+\tau_2+\tau_3))C''(\tau_2) \\ & + (C''(\tau_1) + C''(\tau_1+\tau_2))C''(\tau_2+\tau_3)]C'(0) + [C''(\tau_1)C''(\tau_2) + C''(\tau_1)C''(\tau_2+\tau_3)]C'(\tau_3) \}, \end{aligned} \quad (\text{E9})$$

(7)

$$\begin{aligned} & \frac{8i\alpha_4\alpha_2\alpha_1^2}{\hbar^3} C''(\tau_3) \{ C''(\tau_1+\tau_2)C''(\tau_2)C'(\tau_1+\tau_2) + C''(\tau_1+\tau_2+\tau_3)C''(\tau_2+\tau_3)C'(\tau_1+\tau_2+\tau_3) + C''(\tau_1+\tau_2)C''(\tau_2)C'(\tau_2) \\ & + C''(\tau_1+\tau_2+\tau_3)C''(\tau_2+\tau_3)C'(\tau_2+\tau_3) + [C''(\tau_1+\tau_2)C''(\tau_2) + C''(\tau_1+\tau_2+\tau_3)C''(\tau_2+\tau_3)]C'(\tau_3) \\ & + [C''(\tau_1) + C''(\tau_1+\tau_2+\tau_3)]C''(\tau_2)C'(0) + [C''(\tau_1) + C''(\tau_1+\tau_2)]C''(\tau_2+\tau_3)C'(0) \}. \end{aligned} \quad (\text{E10})$$

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